<Division of Materials Chemistry> Inorganic Photonics Materials

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Visitors

Prof INNOCENZI, Plinio — University of Sassari, Italy, 15 July 2008–1 August 2008
Prof QIU, Jianrong — Zhejiang University, China, 12 June 2008

Scope of Research

In this laboratory, amorphous and polycrystalline inorganic materials and organic-inorganic hybrid materials with various optical functions such as photorefractivity, optical nonlinearity, phptolumionescence and photocatalysis are the target materials, which are synthesized by sol-gel, melt-quenching and sintering methods and so on. Aiming at highly functional materials the structure-property relationship is investigated by X-ray diffraction techniques, high-resoluction NMR, thermal analysis, various laser spectroscopies and quantum chemical calculations.

Research Activities (Year 2008)

Publications

Takahashi M, Uemura K, Maeda T, Yao J, Tokuda Y, Yoko T, Costacurta S, Malfatti L, Innocenzi P: Bottom-up and Top-down Approach for Periodic Microstructures on Thin Oxide Films by Controlled Photo-activated Chemical Processes, *J. Sol-Gel Sci. Tech.*, **48**, 182-186 (2008). (invited paper)

Falcaro P, Costacurta S, Malfatti L, Takahashi M, Kidchob T, Casula M F, Piccinini M, Marcelli A, Marmiroli B, Amenitsch H, Schiavuta P, Innocenzi P: Fabrication of Mesoporous Functionalized Arrays by Integrating Deep X-ray Lithography with Dip-pen Writing, *Adv. Mat.,* **20(10)**, 1864-1869 (2008). (Featured on "Advances in Advance")

Presentations

Takahashi M, "Patterning Technology for Sol-Gel Films", ISGS Sol-Gel School "Sol-Gel in Small Dimensions", Italy, 24–27 August 2008 (invited).

Takahashi M, "Self-oraganized Fabrication of Microstructures on Sol-Gel Derived Films", Deajion, Korea, 3–6 December 2008 (invited).

Tanaka Y, Tokuda Y, Takahashi M, Yoko T, "Preparation of the Durable Organic-inorganic Hybrid Silicophosphate Glasses", Annual Meeting of The Ceramic Society of Japan, 20–22 March 2008.

Grants

Yoko T, Grants-in-Aid for the Scientific Research from Japan Society for the Promotion of Science, No. 20613007.

Development of Alternating Copolymers of Organically-Modified Oxides Prepared by Nonsolvent Condensation

Organic-inorganic hybrid materials are potential candidates for use in the fabrication of electronic and photonic devices with high functionality because these materials can be processed easily and have a high solubility of functional molecules. Recently, an organic-inorganic silicophosphate hybrid has been obtained under a nonsolvent, catalyst-free, low-temperature, one-pot condition by using orthophosphoric acid and organically modified chlorosilane. The following acid-base reaction (metathesis) took place: Si–Cl + P–OH → Si–O–P + HCl↑. The starting materials were mixed and heat-treated at low temperature. The resultant viscous liquid was cooled down to an ambient temperature, producing a transparent bulk hybrid material that provided an alternating polymerized silicophosphate structure with a high homogeneity at the atomic level. The crack-free bulk hybrid material was easily obtained because of the absence of solvent evaporation. However, this reaction produces HCl gas, which is both toxic and caustic. Additionally, the residual HCl gas in the hybrid material may act as a catalyst for the hydrolysis of Si–O–P bonding, resulting in low durability. Thus, the silicophosphate hybrid prepared by the acid-base reaction is not durable.

In this study, we will develop another class of low-melting silicophosphate hybrid formation reaction that is based on nonsolvent alcohol condensation without HCl production: Si–OEt + P–OH → Si–O–P + EtOH↑. The chemical durability of the hybrid was higher than that of the hybrid prepared by using the acid-base reaction. We also investigated the transition state structure of the hydrolysis. It was found that the residual acid assisted the hydrolysis of the hybrids. On the basis of this result we concluded that the durability improvement was performed because of no residual acid in the hybrids prepared by alcohol condensation.

Self-Organized Nanocrystalline Organosilicates in Organic-Inorganic Hybrid Films

Organic-inorganic hybrid films containing organosilica nanocrystals have been obtained by an aqueous process from an organically modified mono-functional alkoxide. Kinetically controlled self-organization was used to design the hybrid nanocomposite films; nanocrystals of around 100 nm in diameter and 4 nm in thickness formed in transparent hybrid films. The layered nanocrystals was found to be oriented within the films which exhibited an optical anisotropy ($\Delta n > 10^{-3}$). Therefore, the hybrid nanocomposite material is thought to be suitable for micro/nanofabrication by soft lithography. In fact the hybrid nanocomposite films with different patterned microstructures have been obtained.

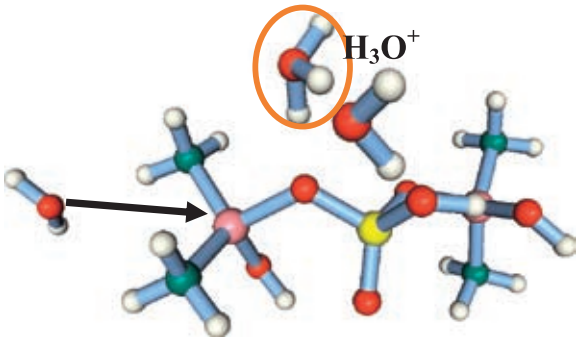

Figure 1. A transition state structure of the hydrolysis of the silicophophate hybrid. The geometry optimization was performed at B3LYP/6-31G* level. It has been found that the oxonium ion promotes the hydrolysis of this model cluster.

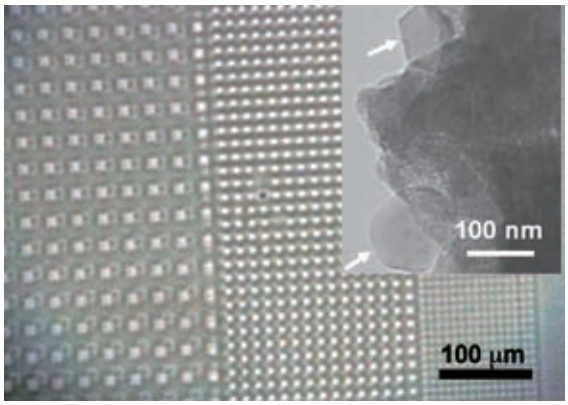

Figure 2. Optical microscope image of the patterned hybrid film containing the layered organosilica nanocrystals micro-fabricated by a soft-lithography. Inset shows TEM image of the corresponding patterned film, in which nanocrystallites are indicated by arrows.

Tokuda Y, CASIO Science Promotion Foundation, December 2007–November 2008.

Tokuda Y, Murata Science Foundation, July 2008–March 2009.

Award

Takahashi M, Award for Promising Young Researchers, The Ceramics Society of Japan, Kansai Branch, 24 July 2008.